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REMARKS ON SPECTRA OF STILBENE DERIVATIVES

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ABSTRACT

Substitution effects on stilbene spectra are predicted by first-order perturbation theory. The intensity increments in the strong first transition should be, and are, additive for different substituents. The observed effects show that the transition is certainly even-odd.

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Application of first-order perturbation theory¹ to the spec-

¹ J. R. Platt, J. Chem. Phys., 19, 263 (1951).

tra of stilbene derivatives as given by Beale and Roe² leads to some

² R. N. Beale and E. M. F. Roe, THIS JOURNAL, _____.

important conclusions. For an allowed even-odd transition in a centrally symmetric molecule, such as the longest-wavelength transition in trans-stilbene, the oscillator strength is the square of a transition moment vector, M.³ A small perturbation by a substituent, a, at

³ R. S. Mulliken and C. A. Rieke, Rep. Prog. Phys., 8, 231 (1941).

a particular position introduces an additional perturbation vector, m_a. The total intensity becomes the square of the vector sum, M + m_a. If there is an angle, θ_a , between the vectors, the oscillator strength in suitable units is

$$f = (M + m_a \cos \theta_a)^2 + (m_a \sin \theta_a)^2$$

$$= M^2 + 2Mm_a \cos \theta_a + m_a^2$$

and the increment is

$$\Delta f = 2Mm_a \cos \theta_a$$

if m_a is relatively small.

For two substituents at opposite positions, the perturbation vectors will be parallel, and the intensity increments will add linearly. (For an even-even transition, they would subtract. For a forbidden even-odd, where M is zero, the perturbation vectors would add linearly, but the intensity increments would go up as the square of the vector sum.⁴) For two substituents at any positions, the total intensity in-

⁴ J. R. Platt, J. Chem. Phys., 19, 000 (1951).

crement will be approximately the sum of the independent increments, in this first-order theory, as long as m_a and m_b are small compared to M .

Examination of Beale and Roe's f -values in the light of these remarks leads to the following conclusions.

1) The longest-wavelength singlet-singlet transition in trans-stilbene is necessarily even-odd (in agreement with all theoretical predictions and with the high intensity). Reason: the 4-methylstilbene intensity is greater than that of stilbene; and the 4,4'-dimethyl intensity is greater still (in arithmetic progression), and not less.

2) The $N(CH_3)_2$ perturbation is larger than the methyl (as noted by Beale and Roe) and in addition it has the same sign. Reason: the 4,4' increments for these substituents add, and do not subtract. The same result has been found⁵ for these substituents as they affect the

5 J. R. Platt, unpublished.

benzene 2600 Å. bands; but the $N(CH_3)_2$ group had a relatively larger effect there.

3) The angle θ for position 3 is almost 90° . Reason: a methyl group in this position produces little change in intensity.

The effect of substituents in the 2-positions, which probably produce steric hindrance, may be treated by the same perturbation theory, as long as the changes in intensity are relatively small. However, the perturbation vectors in this case are no longer necessarily coplanar with the perturbation vectors produced by substituents at other positions.

These general theoretical conclusions support and validate Beale and Roe's important experimental demonstration that in a strong transition the intensity increments from substituents in particular positions are additive.

Independent determination of \underline{m}_a and θ_a at particular positions does not seem feasible for strong transitions (though it can be done for forbidden transitions⁶). If we assume \underline{m}_a constant for a given sub-

6 J. R. Platt, "Electronic Structure and Excitation of Polyenes and Porphyrins", Ch. 4 of Vol. III of Radiation Biology, ed. by S. Hendricks, McGraw-Hill (New York: 1951).

stituent at all positions, θ_a can be approximately determined from the intensity increments except for an ambiguity of sign.

I am indebted to Drs. Beale and Roe for showing me their manuscript in advance of publication.